

naphthylamine, alkylated diphenylamines and unsymmetrical diphenylhydrazine are typical amine-type antioxidants. Tetramethyldiaminodiphenylmethane is an effective antioxidant at temperatures above 100°C where many other amines are ineffective. Among the phenolic compounds, hydroquinone, β -naphthol and alizarin show inhibitory action. However, the most commonly used antioxidants are substitution derivatives of phenol, such as 2,6-di-*tert*-butyl-*p*-cresol, *o*-cyclohexylphenol, and *p*-phenylphenol.

Lubricating oil containing a small amount of dissolved sulfur is effectively inhibited, but is quite corrosive toward copper and its alloys. However, if an organic compound of sulfur is added, inhibition may be achieved without corrosion. Suitable compounds can be produced by reacting sulfur with unsaturated esters such as sperm oil, or with other unsaturated organic compounds such as terpenes and polybutenes. Similar compounds may also be prepared by the reaction of chlorinated wax with sodium sulfide. The products of these reactions are complex, and the sulfur is present in a number of forms such as sulfides, disulfides, etc. Aromatic and aliphatic sulfides, such as dibenzyl sulfide and alkylated diphenyl sulfide, are sometimes used.

Some selenium derivatives are also excellent antioxidants. Dicetyl selenide gives much greater inhibition than the corresponding sulfur compound. Dilauryl selenide is particularly useful for temperatures above 100°C.

Like sulfur, elementary phosphorus is an effective antioxidant, but is too corrosive for actual application. The most common phosphorus-containing antioxidants are alkyl and aryl phosphites such as tributyl phosphite and tris (*p*-*tert*-amylphenyl) phosphite. Naturally occurring phosphorus compounds such as lecithin are also used.

Compounds containing both sulfur and phosphorus have been used extensively as antioxidants. In general, inhibitors containing both elements are definitely superior to those containing only one. Most of the phosphorus-sulfur inhibitors are produced by the reaction of high molecular weight alcohols or unsaturated organic compounds with phosphorus pentasulfide. The alcohols (such as lauryl alcohol, cyclohexanol or butyl phenol) yield dithiophosphoric acids, which are used in the form of their barium, calcium or zinc salts. Phosphorus pentasulfide reacts with terpenes, polybutenes, unsaturated fatty acids and esters, and so forth to give an almost unlimited number of complex addition products.

There are also some organic compounds containing sulfur and nitrogen which are excellent antioxidants. A number of polyvalent metal dithiocarbamates give good inhibition. Phenothiazine is at present the antioxidant most generally employed in diester synthetic oils.

Naturally, the effect of any antioxidant will vary greatly with the nature of the lubricant in which it is used.

Since autooxidation apparently proceeds by a free radical chain mechanism, antioxidants are considered to function by breaking the chain. Thus, the reaction of one molecule of antioxidant

with a chain carrier serves to prevent the oxidation of hundreds or even thousands of lubricant molecules. When the inhibitor reacts, it may be oxidized to a compound which no longer will inhibit oxidation, it may be oxidized to a compound which is a less potent antioxidant, or it may be regenerated. The latter type is, of course, the most desirable. Phenothiazine apparently owes its great inhibitory power to a regenerative reaction which converts active peroxide oxygen to a less active form.

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Cross-references: *Additives, Lubricating Oils*

For Food Products

Antioxidants are chemical compounds which retard oxidation and thus increase the shelf life of foods. Nature was the first to use antioxidants in her storage problems. The tocopherols occur in many fruits, nuts, vegetables, and meats where they may prevent oxidation. Hog fats contain from 1 to 3 parts of tocopherols per 100,000, while the vegetable fats contain from 30 to 100 parts per 100,000. The addition of from 1 to 10 per cent of certain vegetable fats to lard increases the stability of the lard three- to five-fold. The preserving action of the spices, especially rosemary and sage, may be explained by the antioxygenic activity they possess. Preservation of meat by smoking is known to be due to the aromatic compounds in the smoke. Another natural product, ascorbic acid, has been claimed to have antioxygenic activity, but this effect has not been well established. The use of natural and artificial antioxidants has increased materially since the Food and Drug Administration (FDA) has permitted the addition of certain compounds to certain foods. As a rule the most powerful antioxidants are phenolic compounds such as hydroquinone, nordihydroguaiaretic acid (NDGA), butylated hydroxyanisole (BHA), norconidendrin, gum guaiac, and the tocopherols.

Synergists have no antioxygenic value in themselves, but they increase the effectiveness of any natural or artificial antioxidants in the food. Certain acids are known to act in this capacity. Ascorbic, citric and phosphoric acids, the monoesters of ascorbic and fatty acid esters of citric acid, are frequently used as synergists. Ascorbic acid may retard oxidation slightly because it is a reducing agent which may consume part of the dissolved oxygen or reduce the oxidation-reduction potential. Certain compounds such as citric acid and sorbitol act as chelating agents for the removal of metals, such as copper and iron, which promote oxidation.

The concentration of antioxidants approved by the FDA varies with the product but the maximum is 0.02 per cent. Some compounds are effective in concentrations as low as 0.0025 per cent. Any food product containing an added antioxidant must be so labeled.

Some antioxidants have certain properties not possessed by the others. For example, BHA and gum guaiac carry through the heat treatment of baking better than some of the others. Because of

the difference in properties, mixtures of antioxidants and synergists are often used.

The prevention of oxidation in animal products such as fish, meats, and poultry, is of great economic importance, but unfortunately success in this field has been limited, probably because of the poor contact of the antioxidant with the fat and the presence of moisture. The oxidative discoloration of many fruits and vegetables has been retarded by treatment with ascorbic acid. This compound may play three roles in retarding oxidation. They are its action as a reducing agent, acid, and synergist. The discoloration of canned mushrooms has been reduced and the flavor improved by the addition of ascorbic and citric acids.

Antioxidants are used to prevent oxidation of the vitamins. α -Tocopherol (vitamin E) and ascorbic acid (vitamin C) are often added to prevent oxidation of vitamin A.

New antioxidants are being tailormade to meet certain problems in food preservation.

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Cross-references: Additives, Foods, Oxidation

ANTIOZONANTS

Antiozonants, sometimes referred to as "anti-oxidants" and as "sunproofing agents," impart to natural rubber and synthetic rubber compounds various degrees of resistance to atmospheric ozone. The cracking of rubber on exposure to the atmosphere is caused by two separate mechanisms. Light-activated oxidation results in a resinification of the surface; the surface, being brittle, breaks in an irregular criss-cross pattern as a result of surface shrinkage or movement caused by contraction and expansion or other disturbances. The second mechanism is the attack of ozone on strained rubber which takes place in the dark as well as in light and results in cracks running at right angles to the strain. A complex strain pattern will result in a complex crack pattern, but cracking resulting from ozone can usually be identified as being distinct from cracking due to light-activated oxidation.

The atmospheric ozone effect is very often visible in a matter of days, and severe, damaging cracks may develop in weeks. Its action is progressive and once started is not reduced or halted until stress relaxation occurs or the ozone concentration is reduced.

The light-activated oxidation effect is a surface effect which tends to lend protection to the underlying material and is often not particularly disruptive of the rubber's useful life, providing that the article is not thin in cross-section and a high ratio of volume to surface exists.

Petroleum waxes have come to be known as "sunproofing agents" because the cracks in rubber caused by ozone were formerly considered by many to result from exposure of rubber to the sun, and the addition of waxes to rubber compounds tends to reduce or prevent this type of cracking. Waxes are often still referred to in this manner. They function by being incorporated in the rubber in amounts exceeding their solubilities in the

compound so that they migrate to the surface (bloom). This surface layer prevents the ozone from contacting the rubber and thus ozone cracking does not result. A small amount of wax may be more harmful than beneficial, as the surface is spottily coated with wax and where the wax is thin or missing, ozone attack results in large, deep cracks. With no wax, the surface is often uniformly covered with small, shallow cracks which stress-relieve the surface as they form. Wax blooms are often protective for static exposure but if such blooms are lacking in adhesion or flexibility, they will rupture or break away from the rubber surface during dynamic use. This again results in larger and deeper cracks than if no wax had been incorporated.

Waxes used for imparting ozone protection are usually mixtures of microcrystalline and amorphous waxes, some of which are designed to form flexible blooms at winter atmospheric temperatures and yet produce sufficient blooms at the higher temperatures of summer. As temperature rises, the solubility of waxes in polymers increases and thus less wax is available to form the protective bloom. Higher quantities of wax generally help at elevated temperatures, but they may form heavy, crusty, undesirable blooms at normal room temperatures. Paraffin is often effective, but paraffin blooms are generally brittle.

Certain antioxidants, often of the type which provide resistance to flex cracking, also impart added ozone resistance. Some of these antioxidants, when used as antiozonants, must be used in concentrations as high as five parts on the rubber. Often some wax is desirable in the compound to assist in carrying the antiozonant to the rubber surface. Some of these materials also impart dynamic protection which is of concern in such things as tire sidewalls. Representative materials are: (1) secondary aromatic amines such as N,N'-dioctyl-paraphenylenediamine and diphenyl-paraphenylenediamine, and (2) quinoline derivatives such as 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and polymerized 1,2-dihydro-2,2,4-trimethylquinoline.

Certain furane derivatives have also been shown to have antiozonant properties; and for many years it has been known that vulcanized oils, generally known as factice, when used in relatively high loadings, impart ozone resistance, but at the expense of lowering most physical properties. All the materials referred to above are properly called antiozonants as they protect from ozone, as already described.

Reduction of light-activated oxidation effects can be obtained in two ways. Incorporation of opaque ingredients in the rubber will lessen penetration of ultraviolet energy into the rubber and thus reduce the thickness of the oxidized layer. Carbon blacks, certain colors and titanium dioxide act as light shields in this manner. Black compounds resist light-activated oxidation fairly well, but nonblack compounds will generally surface-deteriorate on exposure. The incorporation of antioxidants in rubber compounds will reduce light-activated oxidation effects to some extent. The use of nickel dibutyl dithiocarbamate appears